Paleoceanographic Conditions During the Formation of Fe-Mn Crusts from the Pacific Ocean: Biostratigraphic and Compositional Evidence

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Introduction

Hydrogenetic Fe-Mn crusts play an important role in marine mineral-deposit research because of their widespread occurrence and high concentrations of valuable and rare metals. Most Fe-Mn crust deposits occur on the tens of thousands of seamounts found in the global ocean as well as on ridges and plateaus. Because of these circumstances, it is essential to clarify a number of outstanding issues with regard to Fe-Mn crust history and development, including controls on metal sources and concentrations. The first-order characteristics of Fe-Mn crusts as potential ore deposits include concentrations of metals (grade) and the thickness of crusts (tonnage), which vary depending on Fe-Mn crust structure and texture. Data on the structure, composition, age, and deposit characteristics will help define which factors are key for the creation of mineral accumulation and which combination of factors leads to the formation of potentially economic concentrations of metals.

In this paper, we address the structure and characteristics of Fe-Mn crust stratigraphic sections collected from Central and Western Pacific seamounts. We describe the changes in mineralogical and chemical compositions of crust layers of different ages, the occurrence and regional distribution of these layers that correlate regionally, and reconstruct the paleoceanographic conditions that influenced crust growth.

Methods

Litho- and biostratigraphic methods typically used in stratigraphy and correlation of sedimentary deposits are applied to layered Fe-Mn crusts selected from Western and Central

Pacific seamounts. Samples represent the Hawaiian-Emperor, Line Islands, Mid-Pacific, Marcus-Wake, Marshall Islands, and Magellan seamounts Fe-Mn deposit provinces. Our past research showed that crusts located in different regions of the Pacific Ocean have complementary lithologic and synchronous paleontological changes. Five main crust units define different stages of crust growth: late Paleocene, Eocene, late Oligocene, middle-late Miocene, and Pliocene-Pleistocene [18]. The five crust stratigraphic sections each have distinct and characteristic structure and composition. Clearly, the process of accretion occurs in discrete and discontinuous phases. The more significant hiatuses identified in crust growth are dated as early-middle Oligocene; early Miocene; and early Pliocene.

Texture, and Mineralogical and Chemical Compositions

The upper Paleocene section has a compact, laminated texture showing foliation. The laminae are cut by thin (>1-2 mm) veins of carbonate fluorapatite (CFA). The Eocene and upper Oligocene section is characterized by a mottled texture. Mottling is produced by the presence of non-metal-oxide inclusions, which can be up to 10-15% of the Eocene section and 20-25% of the Oligocene section. The mottles consist of a phosphatized nanno-foraminiferal material. The degree of phosphatization of the nanno-foraminiferal material is much lower in the Oligocene part of the section. The middle-upper Miocene section is characterized by metal oxides showing increased porosity, columnar texture, and infilling of the porosity by clay-sized material (up to 30%). The Pliocene-Pleistocene section has a massive texture with densely packed, vertically oriented columns.

Hein et al. [12] suggested that the extremely fine and compact lamination in crusts results from slow growth rates under oxic conditions with more quiescent bottom-water activity. Intensified bottom-water flow is required for the formation of columnar (pillar) and botryoidal crust textures.

Fe-vernadite and Mn-feroxyhyte are the predominant minerals composing all sections of the crusts [17]. At the same time, the abundance and composition of the non-oxide component in the different stratigraphic sections are different. Phosphates and carbonates dominate in the upper Paleocene, Eocene, and upper Oligocene sections. In contrast, the middle-upper

Miocene section is characterized by a wide variety of authigenic and detrital minerals (clays, zeolites, feldspar, pyroxenes, etc.). Quartz is common in the Pliocene-Pleistocene section.

At the base of some crust sections occurs a shallow-water limestone in which the carbonate matrix was impregnated and replacement by CFA and Fe-Mn oxides. The age of this unit is mainly Late Cretaceous. This lowermost unit differs greatly from crusts with asbolane-buserite and hydrogoethite being the dominant minerals [17].

Chemical analysis of major, minor, and rare earth elements (REEs) for individual crust sequences and bulk samples was carried out. Results from correlation matrices and multivariate analyses reveal the presence of four major groups of elements: Mn–Ni–Co–Cu–Ce-Zn, Ba-Zn-Cu-Fe-Bi-Ce-Sr, Al-Si-Fe-Ti, and Ca–P-REE. These groups of associated elements are broadly similar to those reported by Hein et al. [12], Wen et al. [22], Koschinsky and Hein [13], and Ren et al. [19] for Fe-Mn crusts. These statistical associations were interpreted as hydrogenetic, biogenic, detrital, and CFA phases [12; 22]. These four phases occur in most crusts from the Central and Western Pacific, although the constituents of each phase vary somewhat in the different stratigraphic sections.

The older sections (upper Paleocene, Eocene, and upper Oligocene units) are enriched with hydrogenetic, carbonate fluorapatite, and biogenic phases. They are phosphatized and are characterized by high Mn/Fe ratios. Sr, Ba, Bi, V, I, Mo, and REE have maximum concentrations. However, a relatively low major-metal content is notable.

In contrast, younger sections (middle-upper Miocene and Pliocene-Pleistocene units) are not phosphatized, have low Mn/Fe ratios, relatively high Fe and Co contents, and contain more detrital minerals. Concentrations of Si and Al reach their maximum in the middle-upper Miocene section, which agrees with the mineralogical composition. The Pliocene-Pleistocene section is characterized by higher quartz and the Miocene unit by higher clays, feldspar, and zeolites. The relatively high concentrations of Si and Al indicate that formation of the younger units occurred during times of increased weathering, intensification of bottom-water flow, and increased eolian input.

The Upper Cretaceous section is composed mainly of CFA and is characterized by high (much higher than other sections) concentrations of Ba and lower concentrations of major elements. Ba enrichments in Fe-Mn crusts have sometimes been attributed to hydrothermal processes although a biogenic origin is more commonly accepted [1; 12; 23].

The older and younger units differ in concentrations of REEs. The upper Paleocene and Eocene sections show the largest positive Ce anomalies, possibly reflecting the most strongly oxidizing conditions. In the Miocene-Pleistocene sections, the Ce anomaly is smaller than in the Paleocene section. Other REEs in the younger units have higher concentrations than in the older units. At the same time, LREEs are depleted compared with the HREEs. The upper Oligocene section shows the smallest Ce anomalies, which may reflect the lowest oxygen conditions. The Upper Cretaceous section is comprised mainly of phosphate that is depleted in Ce relative to shale, with values normalized to shale as low as 0.4 to 0.7. Marine phosphorites are typically formed under suboxic conditions. It is likely that suboxic conditions characterized the biologically productive zone of the Equatorial Pacific [2], especially around topographic highs with enhanced upwelling.

Geographic Distribution of Characteristic Fe-Mn Crust Stratigraphic Units

Detailed lithostratigraphic and biostratigraphic study of 60 crust samples from different parts of the Pacific Ocean show that the structure of the crust sections varies throughout the region. The more complete sections are found in crusts from the southern part of the area studied. In contrast, crusts from the central and northern parts of the study area are characterized by incomplete sections. Above all, variations in the Eocene section are notable. The complete Eocene section (lower, middle, upper Eocene subunits) is found in crusts from the slopes of seamounts located to the south of about 14 degrees north latitude. Eocene sections in crusts from seamount slopes located to the north are characterized by the absence of middle or/and upper Eocene sections. In many samples from the Markus-Wake guyots, the Eocene section is missing altogether [17; 19]. Upper Oligocene sections are rarely found in the Fe-Mn crusts, but rather occurs in single samples from the large collection of crusts studied from the Magellan guyots (IOAN and Vlinder) and either overlies the upper Paleocene section with pronounced unconformity or is the first layer above the substrate.

To some degree, the stratigraphic sequence is determined by water depth. The more complete sections, characterized by the occurrence of Paleocene through Pleistocene units, were collected from depths of 1800 to 3000 m. As a rule, these are: (1) the summits of guyots, presently located at depths greater than about 1800-2000 m; (2) summit surfaces of satellite volcanic edifices, which are typically 400-500 m deeper than the summit surfaces; (3) subhorizontal terraces, saddles, and spurs along the summit and flanks of guyots. Crusts collected from water depths of less than 1800 m as a rule have incomplete sections, with the upper Paleocene and/or Eocene units being absent.

Extensive sampling of the Magellan guyots (more than 1000 samples) has made it possible to delineate the detailed distribution of each Fe-Mn crust stratigraphic unit [17; 18]. The greatest volume of Fe-Mn oxides from complete Fe-Mn crust sections is the Eocene and Miocene-Pleistocene units. The frequency of occurrence of Eocene sections on the Magellan guyots varies. For example, on IOAN guyot it occurs in 41% of the samples, whereas on Dalmorgeologia guyot it is found in 32% of the crusts. Miocene units occur in 70% of the crusts collected. The Pliocene-Pleistocene unit occurs in all the crusts sampled, but its thickness can be as little as a few millimeters. The upper Paleocene unit is found only sporadically and does not play a significant role in crust deposit structure.

Based on shallow boreholes drilled with the help of the submersible unit GBU-1.5/4000 on Fedorov and Alba guyots (Magellan Seamounts), the variability of crust thickness is reflected by the variability of their stratigraphic units [16]. Thinner crusts result from the omission of certain stratigraphic units in the sections. Thick crusts typically reflect an anomalous increase in the thickness of the upper Paleocene and/or Eocene units. At the same time, the more complete sections are confined to specific water depths. For example, on Fedorov guyot, the occurrence together of Paleocene, Eocene, and Miocene-Pleistocene units in crusts occurs from terraces and spurs along the upper flank at depths of 2000 to 2400 m. The Paleocene section is absent in some crust sections collected from water depths of less than 2000 m and deeper than 2500 m. The Eocene unit disappears (phases out) from crusts collected at water depths deeper than about 2700 m. On the summit of the guyot at depths of 1800-1500 m, incomplete crust sections were found; their younger part is represented by a Miocene-Pleistocene section and the older part is generally represented by an incomplete Eocene section.

Paleoceanographic and Geological Implications

Complementary lithological, mineralogical, chemical, and paleontological changes, and consistent ages for stratigraphic sequences in crusts collected over large distances indicate that the process of Fe-Mn oxide accretion on the seamounts of the Western and Central Pacific occurred synchronously from the Late Cretaceous through the Pleistocene. Variations in the textures and mineralogical and chemical compositions of Fe-Mn crusts reflect the influence of prevailing environmental conditions at the time of formation of the deposit.

Reconstruction of a sequence of geological and oceanographic events that impacted Western and Central Pacific seamounts and resulted in Fe-Mn crust accretion on seamount rock surfaces can be presented as follows. The Western and Central Pacific seamounts formed during the Cretaceous at paleolatitudes that are equivalent to the present location of French Polynesia [2, 14]. They started migrating in a northwest direction about 110 Ma ago, while experiencing vertical displacement as a result of isostatic subsidence and movement over lithospheric swells, complicated by tectonic rejuvenation. In the Late Cretaceous (Campanian and Maastrichtian), the surfaces of many guyots were submerged deeper than about 100-120 m water depth. It was a period of non-deposition of $CaCO_3$, pronounced erosion and submarine karstification of the substratum, infiltration of fractures and cavities in the shallow-water limestone and volcanic rocks on the guyot's summit with pelagic carbonate, and formation of submarine ferromanganese hardgrounds [2]. Mineralogical and chemical compositions indicate that phosphatization of the Upper Cretaceous Fe-Mn hardgrounds may have taken place under suboxic conditions. It is likely that the suboxic conditions developed in the biologically productive zone of the equatorial Pacific [2].

A period of submarine hardground and insipient crust formation lasted until the late Paleocene and coincided with an oligotaxic ocean characterized by cool oceans and low productivity. The Late Cretaceous-Paleocene mass extinction of species of planktonic foraminifer and calcareous nannoplankton led to a sharp reduction of carbonate accumulation in the Pacific. That time period is marked by a regional hiatus in carbonate accumulation [15].

In the late Paleocene, the stratigraphic crust layers began to grow. Crust formation on Cretaceous seamounts was widespread at that time and may have been intensified when the seamounts migrated into the equatorial belt. According to Bogdanov et al. [2], Fe-Mn crust accretion was initiated when the summit of seamounts subsided below the North and South Equatorial Countercurrents (NECC, SECC) and Equatorial Undercurrent (EUC), where the contemporary current velocities range from 35 to 170 cm/s. The base of these currents occur near 317 m depth for NECC and SECC and at less than 200 m for the EUC, thereby delineating the upper limit for late Paleocene Fe-Mn crust accretion if Bogdanov is correct. This conclusion is consistent with guyot subsidence history, which shows that Fe-Mn crust precipitation was initiated when the summit of the guyots subsided to about 400 m water depth; Fe-Mn crust precipitation continued as the guyots subsided through the Equatorial Intermediate Undercurrent.

Growth of the upper Paleocene and Eocene Fe-Mn crust sections were associated with periods of global Eocene transgression, which corresponded to a time of polytaxic conditions including increased bioproductivity, an expanded oxygen-minimum zone (OMZ), considerable production of biogenic carbonate, a relatively high CCD, and high calcium-carbonate dissolution rates, which may have increased the Fe oxyhydroxide component in the water column [7].

The OMZ played a key role in the acquisition of metals from seawater and in other chemical processes [7, 10]. Crusts of late Paleocene and Eocene ages may have formed within the relatively shallow-water part of the OMZ in the equatorial zone of high bioproductivity [2]. In the early Eocene, the northern group of guyots of the area studied was located at paleolatitudes of about 13°-14° N. In contrast, the southern group of guyots was located at about 4°-2° S paleolatitudes and remained in the equatorial high-productivity zone for most of their history. The geological timing of the passing of a seamount through this equatorial zone may explain the differences in the structure of the Eocene metal-oxide sub-units described above.

The Eocene-Oligocene boundary is marked by a global biota crisis [15], a consequence of considerable glaciation at high latitudes and global cooling. Widespread extinctions of planktonic microfossils and reduction of a variety of species occurred. Oligocene sediments reflect this low biological productivity and show an early Oligocene regional hiatus in carbonate accumulation. This event correlates with the hiatus in Fe-Mn crust accretion. The early-middle Oligocene hiatus in crust growth found in all samples studied coincides with an oligotaxic ocean. This oligotaxic period was characterized by colder oceans, a relatively deep CCD, low dissolution rates of planktonic calcium carbonate, and insignificant Fe oxyhydroxide supply to the water column.

Detailed biostratigraphy of Fe-Mn crusts and analysis of paleoceanographic events show that at the end of Oligocene conditions again became favorable for the accretion of crusts, which is reflected in the formation of the upper Oligocene section. According to the Vail curve, that time was marked by rising sea-level [21], increasing water temperature [24] and bioproductivity, with an insignificant increase in CCD depth and calcium-carbonate dissolution rates.

Processes of phosphatization of the upper Paleocene-Eocene and upper Oligocene crust sections were related to two major episodes of phosphogenesis in the late Eocene/early Oligocene (~24 Ma) and late Oligocene/early Miocene (~24 Ma) and a minor episode in the middle Miocene at ~15 Ma [11].

By the middle Miocene, guyots of the area studied were located at paleolatitudes closer to their modern positions and the summit surfaces reached depths close to their contemporary ones. During the Miocene, glaciation was widespread and [15, 6] by 15 million years ago the size of the Antarctic ice shield increased considerably. Climate contrasts increased between the poles and the equator, which led to increased mixing of surface and subsurface waters, as well as to an increase in nutrients supplied to plankton. These conditions promoted a resumption of evolutionary radiation. At the beginning of the middle Miocene, biological productivity increased sharply. The middle Miocene was also the time when of the accretion of the younger crust sections began. Chemical analyses of crusts show Si and Al enrichment in these younger layers, suggesting intensification of weathering, increased bottom-water flow, and an increased influx of wind-borne particles by trade winds from the Asian continent [2, 12, 19].

The youngest crust sections formed within and below the deeper-water OMZ, a generally low-productivity zone, while the older crust units, according to Bogdanov, formed within the relatively shallow-water OMZ in the equatorial zone of high bioproductivity [2]. These proposed water-depth differences may in part have controlled the composition of the different aged crust units. This assumption can be conditionally illustrated by a N–S profile of the OMZ across the equatorial Pacific, which shows that the level of the OMZ changes southwards [6, 20]. In the south, the OMZ is located at a shallower depth and in the north at greater depths. The present-day distribution with latitude was probably the same as in the past, but the relative levels were likely different.

Conclusions

The chronostratigraphy of Fe-Mn crusts delineates condensed stratigraphic sequences that reflect the stage-by-stage accumulation of metals from the Late Cretaceous through the Quaternary, with hiatuses in growth between intervals of metal deposition.

The main periods of crust accretion were associated with periods of global transgressions, which corresponded to times of polytaxic conditions including: (1) warm oceans, (2) a relatively high CCD, and (3) high carbonate dissolution rates, which according to Halbach [7] may have increased the Fe oxyhydroxide component in the water column. Hiatuses in crust growth coincided with an oligotaxic ocean characterized by colder waters, low productivity, low dissolution rates of planktonic calcium carbonate, and insignificant Fe oxyhydroxide supply to the water column.

In addition, the structure of the Fe-Mn crust sections reflects the geological evolution of the seamounts on which Fe-Mn oxides accreted. Favorable conditions for Fe-Mn oxyhydroxide/oxide accretion on the slopes of seamounts was determined by their history of submergence, crossing the equatorial zone of high bioproductivity by plate tectonic movement, chemical composition of the water masses, pole-to-equator thermal gradient and oceanic mixing, extent and intensity of the OMZ, and rates of oxide accretion, among others.

Fe-Mn crusts form pavements on the subhorizontal surfaces of seamount flanks and summit. Those pavements can be continuous over large areas where the seamount flanks and summit have been swept clean of sediments by bottom currents for millions of years. Thicker crusts consist of both older and younger crust growth units. Thick crusts are well developed at:

(1) the summit of guyots, whose modern bathymetric level is about 1800-2000 m or more; (2) the summit of satellite volcanic edifices, located at water depths of about 400-500 m below the summit surfaces of the main edifices; (3) subhorizontal terraces, saddles, and spurs along the upper flanks and summit.

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